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THE APPLICATIONS OF THERMODYNAMICS TO CHEMISTRY.

Traité élémentaire de Mécanique chimique, fondée sur la Thermodynamique. Par P. Duhem. 4 vols. Vol. i. pp. viii + 299; vol. ii. pp. 378; vol. iii. pp. 380; vol. iv. pp. 381. (Paris: Librairie scientifique, A. Hermann, 1897–1899.)

PROF. DUHEM'S treatise on the thermodynamic potential is so well known that little or nothing need be said in introducing another work from the pen of the same writer dealing with thermodynamical considerations.

The study of the laws of combination and dissociation is intimately connected with that of such physical processes as evaporation, liquefaction and solution. To this subject the not over-appropriate title of "chemical mechanics" (*mécanique chimique*) has been given in France. While Berthollet sought an explanation of the fundamental phenomena in the laws of motion combined with the Newtonian hypothesis of molecular attractions and repulsions, Sainte-Claire Deville referred the principles of "chemical mechanics" to thermodynamical considerations, and thanks to the labours of Hortsmann, Moutier, Gibbs, Helmholtz and a large number of other physicists, there has sprung up that wide field of investigation which has given the present book its title of "chemical mechanics founded on thermodynamics," or more briefly, chemical thermodynamics.

It is not with special applications alone that Duhem deals. The greater portion of the first volume and part of the second are occupied with thermodynamics proper, and constitute, to our mind, the best treatise on thermodynamics that we have seen. An introductory section contains a summary of the more important mathematical and dynamical theorems and principles required at the outset, and this should be helpful to students.

In his preface the author calls attention to the great difficulty of giving a perfectly rigorous and logical exposition of the laws of thermodynamics, and claims only to have attained the degree of precision usually adopted in treatises on physics. A comparison of Duhem's work with the heterogeneous mixtures of experimental results, mathematical formulæ and veiled assumptions which commonly have to do duty as text-books on thermodynamics, will show that the author has really advanced a long way in making the subject clear and intelligible. No better illustration of this can be cited than the careful precautions taken to avoid premature assumptions with regard to thermometric scales in the treatment of perfect gases. In these days of widespread education in "general elementary science" such terms as "a perfect gas" and "absolute temperature" bid fair to become by-words; but how many B.Sc.'s either of London or of our provincial universities can give correct definitions of them? If this point were tested, we venture to predict that in the vast majority of cases the first term would be defined by reference to the second, and the second by reference to the first, and if the circular nature of this reasoning were pointed out, the graduate under examination would have to take refuge in considerations respecting molecules, about whose nature and mode of motion he knew nothing. Moreover, apart from Charles's law and the difficulties connected with it, comes the question as to whether or not the definition of a perfect gas is to include Clausius's hypothesis as to the constancy of one (and therefore both) of the specific heats. Here again the question is considered most explicitly.

Another feature of Duhem's treatment is that while the old familiar p, v, t trio receives full consideration, generalised coordinates are introduced from the very outset, and the significance of such coordinates is explained by illustrative examples as far as possible. To one feature, however, we must take exception, and that is the retention in Duhem's equations of the useless E (synonymous with the English J) standing for the "mechanical equivalent of heat," as it was once, and unfortunately often still is, called. This quantity is nothing more or less than the work measure of the specific heat of water at a certain temperature, and the equations of thermodynamics in no way depend on the specific heat of water. The absolute unit of heat is the unit of work, and with this unit E must be replaced by unity. As Prof. Poynting remarked in his address to Section A at Dover, "the real superiority of the work measure of specific heat lies in the fact that it is independent of any particular substance, and there is nothing whatever hypothetical about it."

In this respect the work unit of heat stands on a much more rational footing than the universally adopted dual systems of so-called "absolute units" of electricity and magnetism, which are not independent of the medium, and whose dimensions moreover are incompatible.

As regards Duhem's two chapters on stability, we can only wish they had been before us when first learning thermodynamics, as we should have been saved the trouble of thinking out for ourselves conclusions similar to those here expounded, after vainly attempting to follow the arguments of the text-books and to apply them to a Tripos rider; now the whole matter appears before us in a clearer light than it ever did previously.

The last part (Book ii.) of volume i. deals with false equilibria and explosions. By "false equilibria" (*faux équilibres*) are meant states of equilibrium which can be realised experimentally, although the conditions of equilibrium of conventional—or, as Duhem calls it, "classical"—thermodynamics are not satisfied. They are analogous to the equilibrium of rough bodies in statics, in configurations which, in the absence of friction, would have been impossible. This analogy has led, in Duhem's hands, to the development of an extremely elegant mathematical theory of false equilibria and explosions based on the introduction of a function which the author calls the "friction" (*le frottement*) of the system. This function is entirely distinct from that which represents viscosity, but when it is introduced into the equations of the system, along with the thermodynamic potentials, Clausius's inequality for irreversible cycles $\int dQ/T > 0$ is satisfied. In a diagrammatic representation, the line of true equilibrium is bordered on either side by a region of false equilibrium. When the representative point just falls outside this region the conditions required for the occurrence of an explosion admit of a simple geometric interpretation.

In the second volume, Book iii. deals with change of state, dissociation, and the triple point; much of the latter matter will be familiar to those who have read the author's "Thermodynamic Potential." Book iv. deals with the critical point, the principle of James Thomson, Van der Waals's and allied formulæ, and the principle of corresponding states, specific heats of fluids, and adiabatic expansion of vapours. Book v. treats of dissociation in mixtures of perfect gases. In the third volume, Book vi. deals with the thermodynamic potentials of a homogeneous mixture, solution, osmotic pressure, the hypotheses of Van 't Hoff and Arrhenius, and the law of Guldberg and Waage. Book vii. contains a full investigation of the general problem of solution, the chapter dealing with double salts being of much interest, especially the graphical representations. In the fourth volume Book viii. is devoted to the consideration of double mixtures, including the thermodynamic theory of distillation, while an account of Willard Gibbs's theory of the statics of heterogeneous systems in Book ix. concludes the treatise. In this last book the law of phases is established, and the different degrees of variance of a system are considered separately, actual instances of the systems in question being cited. A separate chapter is devoted to the properties of univariant and bivariant systems. As Duhem points out, the whole of this theory is based on "classical" thermodynamics where "friction" is left out of account, as is also capillary action.

The treatise, taken as a whole, shows what vast progress has been made in expressing the laws of mixture, combination, dissociation, and chemical transformation generally, in terms of a single potential function of generalised coordinates, and thus placing chemistry and chemical physics on a similar footing to dynamics. The essentially mathematical treatment is not the least valuable feature of Duhem's work. Thermodynamics is quite as capable of being regarded from a purely mathematical standpoint as dynamics or hydrodynamics, but hitherto its mathematical aspect has not been exhibited so prominently as it ought to be. The inclusion of descriptions of details of experiments would have broken the continuity of the theory, and such details can be far better studied in the original papers to which abundant references are given in footnotes. Indeed, the present work appears to be in many respects a model of what such a treatise ought to be. In any special problem certain hypotheses are first made; these should be clearly pointed out, and attention specially drawn to them. From these hypotheses certain conclusions are drawn by mathematical reasoning, and lastly we have references to the evidence derived from experiment as to the accordance of these conclusions with observed facts. So long as a substance is regarded as a purely mathematical abstraction, it may be defined by any hypotheses whatever as to the form of its thermodynamic functions, and a Thermodynamics based on hypotheses convenient for purposes of calculation would possess the same interest to mathematicians as a Hydrodynamics which ignores viscosity and capillarity or a Geometry of any particular non-Euclidian space. But it would appear that the conclusions *do* largely represent, either exactly or as approximations, the results of experiment; and the subject thus assumes a physical reality.

It is difficult in writing on such a subject as the present to avoid, quite unintentionally, "smuggling" doubtful assumptions into the midst of an argument without declaring their nature. As we all know the late Clerk Maxwell was much addicted to this practice, the gaps in his reasoning having afforded fruitful material for later investigators. When we consider the variety of sources from which the subject-matter of the present treatise has been compiled, we can only congratulate the author on the measure of success he has achieved in admitting only perfectly rigorous deductions based on explicitly stated hypotheses.

We cannot close this work without some reflections as to the relative progress that has been accomplished by the two schools in explaining the properties of matter, the one by means of the thermodynamical potential, and the other by the application of dynamical principles to the individual molecules of bodies. Molecular dynamics has given us equations representing, under certain conditions, the fact that dQ/T is a perfect differential; but there is still a something we have not got to the bottom of in every kinetic theory of matter, as applied to thermodynamics. We have as yet discovered no dynamical theorem of sufficient generality corresponding to the uniqueness of temperature, or establishing the fact that under the most general possible conditions the entropy of a system tends to a maximum. The question—Can the irreversible phenomena of thermodynamics of a body of finite size be accounted for by applying the equations of a conservative and reversible dynamical system to its individual molecules without making *some* special assumptions?—has never been completely answered. To deduce the second law from the equations of the kinetic theory imposes restrictions on the systems to which the conclusion applies where no such restrictions exist in the law itself. Even the very question of applying statistical methods at all to systems of molecules endowed with the property of perpetual motion requires careful consideration, since our statistical theories are so largely based on our experience of every-day phenomena—events by their very nature irreversible. One may thus be led to wonder whether Prof. Duhem's "friction" may possibly involve the existence of some molecular property which prevents molecular motions from being represented by the equations of what in the author's own nomenclature may be styled "classical" dynamics, and which introduces irreversibility into the motions even of individual molecules.

From a mathematical point of view the theory of the thermodynamic potential has attained far greater perfection than any theories based on molecular hypotheses that have been suggested up to the present; whatever the future may bring forth is another question. While thermodynamics originated in this country from the discoveries of Joule, it now hardly receives so much attention from Englishmen as it deserves. Prof. Duhem's treatise, by showing the wide range of phenomena which come under its scope, even omitting (as he does) thermo-electric phenomena and thermo-elasticity, cannot fail to attract students to this fascinating branch of mathematical physics. G. H. Bryan.

THE CONTINUITY OF THE ERYTHREAN RIFT VALLEY.

Seconda Spedizione Bottego. L'Omo. Viaggio d'Esplorazione nell' Africa Orientale. By L. Vannutelli and C. Citerni. Pp. xvi + 650; 11 plates, 9 maps, and numerous illustrations. (Milano: Hoepli, 1899.)

THE Erythrean Rift Valley has been proved continuous across forty degrees of latitude from the Jordan to the south of Kilima Njaro, except for a possible break of about 250 miles between Lake Rudolf and the basin of the Hawash. Whether the valley is broken in that district depends on the course of the Omo and its relations to the river known as the Nianam, which flows into the northern end of Lake Rudolf. The name Omo was introduced into geography by Léon des Avanchers in 1858, for a river which drains part of the southern slope of Abyssinia, a little to the west of Menelik's capital at Addis Abeba. The river had been known long before, for it is the Zebé of the seventeenth-century Jesuit missionaries. The upper part of its course was described by Ludolf in his "New History of Ethiopia" (1681) from information supplied by the Abba Gregorius. But the lower course of the river was quite unknown. Ludolf believed that it flowed eastward and entered the Indian Ocean near Mombasa.

Bruce in the following century accepted this hypothesis and called the river the "Zebé or Quilimancy," the latter being an old name for the Ozi, a river which is a parasite of the Tana.[1]

But in the present century Frederick Ayrton and Antoine d'Abbadie claimed the Zebé as one of the head-streams of the Nile. This view was supported by Petermann, who held the Zebé to be a tributary of the Sobat, and by Bonala, who believed that it flowed into the Victoria Nyanza, and was therefore the remotest source of the Nile. Harris, McQueen, Schweinfurth and Cecchi on the contrary supported the theory that the Zebé belonged to the Indian ocean drainage, and rendered this view more plausible by identifying the Omo as one of the sources of the Juba. In 1889 and 1890 a fresh explanation was introduced by Teleki and von Höhnel's discovery of Lake Rudolf, and Borelli's descent of the Omo towards that lake, into which native rumour asserted that the river flowed. The work of these travellers seemed to disprove both the old theories; but Dr. Donaldson Smith, after his important journey to Lake Rudolf in 1895-6 again advocated the connection of the Omo and the Juba. What was known of the levels of the three rivers seemed fatal to this idea, and in a review of Donaldson Smith's book in Nature (July 1, 1897) it was maintained that the Omo and the Juba could not be connected, and that "the Omo must continue as the Nianam and flow into Lake Rudolf."

In order to settle this long controversy Vittorio Bottego, an explorer well known from his work in the Juba basin in 1891-2, proposed an expedition which was fitted out under the auspices of the Italian Geographical Society. Thanks to the energy of this Society, Bottego started in October 1895 from Barawa on the Somali coast at the head of a powerful caravan of four European officers, 250 natives, 120 camels, and 300 mules.

The expedition left Barawa in October 1895, and marched across Italian Somaliland, along a route parallel to the river known to geographers as the Juba. The authors, however, speak of it as the Fiume Ganana, which being interpreted is the "River River."

The first long halt was at Logh, the principal commercial centre in the Juba valley. After building a fort and a trading station at that town the expedition crossed the "Fiume Ueb" (which also means "River River"), and marched north-westward up the course of the principal tributary of the Juba. The explorers found that this river dwindled rapidly, and long before they reached its head found that it could have no connection with the Omo. Leaving the Juba basin, the expedition carefully explored Lake Abbaia, which it is proposed to call Lagho Regina Margherita, and then proceeded to its main objective the Omo. The river was reached near the point to which Borelli had tracked it from the north. Bottego, after his former expedition, inclined to the view that the Omo was one of the Nile tributaries; but after following the river for some distance westward it suddenly bent southward, became the Nianam of von Höhnel, and entered Lake Rudolf. The Omo problem was settled.

While resting in the food country at the northern end of Lake Rudolf, the expedition mapped its western shores, and collected much fresh information regarding the Reshiat, who are described under the name of the Gheleba. This interesting tribe was first described by von Höhnel. From the facts and figures given by Vannutelli and Citerni it appears probable that the people are Nilotic negroes, allied to the Njempsians, and altered by Galla intermixture.

After mapping the western shores of Lake Rudolf the expedition proceeded up the second river, which von Höhnel had described as entering the northern end of the lake. The existence of this river has, however, been denied. Bottego's party followed the river, which it is proposed to rename the Fiume Maurizio Sacchi, to the north-west; but its course is short, and the expedition climbed the water-shed into one of the tributaries of the Sobat. For this tributary the authors propose to restrict the name of Juba. They followed this river to the north-west until it left the Ethiopian highlands near its junction with the group of rivers that unite to form the Sobat. They traversed the swamps of this region to a point some forty miles from the old Egyptian station of Nassur. Having thus settled the relations of the Sobat-Juba, the expedition returned to the Abyssinian highlands on the home trail. They entered the Sajo country, which is ruled by one of Menelik's governors. Bottego sent a polite request for permission to return to Massowah either across the Amhara province around Lake Tsana, or through Shoa, or by any route which might be suggested. The expedition was invited to visit the

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[1] Bruce is quoted on p. 4 of the present work as having regarded the Zebé as one of the head-streams of the Nile; but that was only the view of some of his editors. Bruce himself did not reach the Zebé; he does not appear to mention it in his narrative, and his map marks it as separated from the Nile tributaries.